

# INFLUENCE OF COAL TYPE AND DEVOLATILIZATION CONDITIONS ON SULFUR EVOLUTION DURING COAL PYROLYSIS

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## ABSTRACT

Coal derived products via gasification constitute an attractive alternative source of clean fuels and power compared to pulverized coal combustion. It is well-known that devolatilization of coal is the most important event in the initial stages of all coal conversion processes including gasification. Low- and high-sulfur coals were devolatilized in a number of reactors at various peak temperatures. In addition, a brief review of the available literature data in this area has been performed. The results obtained in this study provide further insights regarding the dependence of the nature of sulfur products evolved during devolatilization on feedstock type.

## INTRODUCTION, BACKGROUND AND OBJECTIVES

A fundamental understanding of the physical and chemical transformation of the sulfur present in coal during devolatilization is essential for effective utilization of large reserves of high sulfur coal present in the United States. Coal devolatilization is a key step in various conversion processes including gasification. The organic and inorganic constituents of coal undergo significant changes during devolatilization. The extent of these changes depends on the peak devolatilization temperature, heating rate, gas atmosphere, and most importantly, coal type.

The thermal decomposition of inorganic and organic sulfur in coal forms primarily  $H_2S$ ,  $SO_2$ ,  $CS_2$ ,  $S_2$ , and  $CH_3SH$ , depending on the devolatilization conditions used. Snow (1932) investigated the conversion of coal sulfur to volatile sulfur at various temperatures and in streams of various gases. In these experiments, Illinois No. 6 coal was heated under flowing gases ( $H_2$ ,  $N_2$ ,  $CO_2$ ,  $CH_4$ ,  $C_2H_4$ , and steam) at both slow and (relatively) rapid heating rates. Snow noted that under inert atmospheres, the first traces of  $H_2S$  appeared at about  $200^\circ C$  and that the  $H_2S$  that evolved prior to  $270^\circ C$  account for 0.1 percent of total coal sulfur. Snow demonstrated that the maximum desulfurization achievable under the conditions tested (slow heating rate,  $10^\circ C/min$ ; "long" residence time at the peak temperature) is about 50 percent, and this value is essentially reached by  $600^\circ C$ . Snow also demonstrated that 10 percent of the total coal sulfur is eliminated at  $360^\circ C$ .

In the Texaco Coal Gasification Process (TCGP), devolatilization of coal occurs in the presence of oxygen. Consequently, it is of interest to better understand the influence of oxygen atmosphere on sulfur evolution. Groves, et al. (1987), studied the decomposition of mineral pyrite in air, 2 percent  $O_2/N_2$ , and pure  $N_2$  atmospheres. In these experiments, commercially available samples of mineral pyrite were finely ground and pelletized. The pellets were then placed in a vertical tube furnace with flowing gas atmospheres, and heated for 15 min at temperatures from 300°C to 1,100°C. The decomposition products were analyzed by X-ray diffraction. The results show that pyrite was stable up to 450°C and completely decomposed to form pyrrhotite at 700°C. The pyrrhotite thus formed was stable up to 1,000°C. Above 1,000°C, the pyrrhotite decomposed to form magnetite. The authors also investigated the decomposition of mineral pyrite in a 2 percent  $O_2/N_2$  atmosphere. The authors claim that this atmosphere resembles that of a boiler furnace. In the oxidizing atmosphere pyrite began to decompose at 350°C to form pyrrhotite and haematite. More pyrrhotite and less haematite was formed under these conditions than in an air atmosphere. The final traces of pyrite were detected at 900°C. A maximum amount of haematite was detected at 900°C; above this temperature, haematite steadily decreased while magnetite steadily increased. At 1,100°C, magnetite was the major species present with only trace amounts of pyrrhotite and haematite detected. They also demonstrate that pyrite decomposed to yield pyrrhotite, magnetite and haematite. As the partial pressure of oxygen is decreased, pyrrhotite becomes stable over a larger temperature range, and magnetite is preferentially formed over haematite.

Devolatilization of coal in the TCGP is also influenced by the  $H_2$  atmosphere present in the gasifier. Yergey, et al. (1974), performed nonisothermal kinetic studies on the hydrodesulfurization of coal and mineral pyrite. In these experiments, hydrogen was passed over a finely ground bed of coal placed in a quartz reaction tube. The tube was then placed in a furnace, and the temperature increased at heating rates that varied from 1°C/min to 100°C/min up to temperatures in the range of 27 to 1,027°C. The gas product residence time in the sample bed was determined to be on the order of  $7.5 \times 10^{-2}$  sec. The gases evolved were analyzed by a mass spectrometer. The authors concluded the following: (a) the low-temperature  $H_2S$  peak at 412°C associated with two super-imposed organic sulfur removal processes designated as organic I and organic II; (b)  $H_2S$  evolution peaks observed at 517°C and 617°C associated with the decomposition of pyrite and iron sulfide; (c)  $H_2S$  evolution peaks beginning at 527°C and centered at 657°C associated with hydrodesulfurization of more stable organic sulfur species designated as organic III.

Calkins (1987) flash pyrolyzed various coals to determine the conversion and distribution of products for comparison with data obtained using model compounds. Based on an exhaustive study the following conclusions were drawn: aliphatic and benzylic

sulfides, mercaptans and disulfides are evolved at relatively low temperatures (700°C to 850°C); aromatic sulfides and mercaptans require much higher temperature (900°C) to give high yield of H<sub>2</sub>S; thiophene and its derivative show low yield to H<sub>2</sub>S even at a temperature as high as 900°C.

Khan (1989a) developed models to predict the distribution of sulfur in the products based on pyrolysis data for 32 different coal samples devolatilized in a fixed-bed reactor. Khan observed that the total sulfur content in the pyrolysis products at 500°C could be correlated to the total sulfur (weight percent of original coal) content. Khan also investigated the influence of the peak devolatilization temperature on sulfur evolution during the pyrolysis of a Pittsburgh No. 8 coal. The relationships are as follows:

$$\text{Total sulfur in gas} = 0.31 \times S_{\text{coal}} \\ [R^2 = 0.93, F = 425, P = 0.0001]$$

$$\text{Total sulfur in tar} = 0.06 \times S_{\text{coal}} \\ [R^2 = 0.85, F = 175, P = 0.0001]$$

$$\text{Total sulfur in char} = 0.61 \times S_{\text{coal}} \\ [R^2 = 0.98, F = 1,475, P = 0.0001]$$

where,  $R^2$  = coefficient of determination  
F = mean square of the model divided by the mean square of the error  
P = significance value;  $P < 0.05$  = significant

One of the above correlations was applied to predict the distribution of sulfur in the condensable fraction of the products generated by a fixed-bed gasification process. For the Pittsburgh No. 8 coal, the predicted percent was 6 percent, which compared well with the estimated sulfur content (5 percent) based on the DOE/METC data from the 42-inch fixed-bed gasifier. This finding confirms that the fixed-bed pyrolyzer utilized by Khan provided a reasonable simulation of the top portion of a fixed-bed gasification process.

Khan (1989a) also performed a multivariate analysis to understand the role of sulfur type (e.g., pyritic versus organic) on their distribution. Multivariate analysis demonstrated that the organic sulfur content of coal plays a stronger role in determining the sulfur content of tar or gases. The pyritic sulfur content of the coal on the other hand plays a key role in determining the sulfur content of the char, at the low-temperature devolatilization conditions. With the increase in the peak devolatilization temperature, however, the gaseous sulfur yield increases at the expense of char sulfur. A summary of the correlations developed by Khan is presented in Table 1.

The objectives of this study are to achieve a better understanding of the chemistry of sulfur evolution by (a)

extending the data base over that previously used (Khan 1989a) for coal devolatilization, and (b) utilization of advanced statistical techniques for data analyses.

## EXPERIMENTAL

The details of experimental procedures used in this study are available in the numerous reports published in the literature. The information on devolatilization of coal in a fixed-bed reactor has been described by Khan (1989a, 1989b). A selected number of coals investigated by Khan were also characterized by Curie-point pyrolysis/mass spectrometric (MS) technique at the University of Utah. Curie-point pyrolysis/mass spectrometric technique has been described by Chakravarty et al (1989a, 1989b). During the early 1980s Texaco Inc. commissioned Advanced Fuel Research (AFR) to investigate the devolatilization behavior of a number of coals of interest to Texaco using the AFR's heated-grid technique. In this report devolatilization data on these coals, particularly information on heteroatoms evolved during devolatilization are provided; additional analyses on these data will be reported separately. Information on the heated-grid technique has been widely reported in the literature (e.g., Solomon and Hamblen, 1985).

## RESULTS AND DISCUSSION

### Pyrolysis of coal in a fixed-bed reactor and comparison with Curie-point pyrolysis/mass spectrometric results

Table 2 summarizes the intensity data of selected masses (chosen to contain sulfur containing molecules) in the spectra of pyrolyzed coals (in-situ in the Curie-point pyrolyzer) evaporated tars and the different forms of sulfur analyzed in fifteen neat coal samples. The coals selected are part of a larger set of data used for statistical analyses performed by Khan (1989a).

In order to sort out the fifteen coals in terms of their underlying sulfur forms (organic, pyritic, and sulfate), factor analysis was performed (figure not shown). For the data set considered, samples 6, 8, and 19 contain significant amounts of organic sulfur. Samples 2, 16, 17, and 24 are relatively high in pyritic sulfur (all of them are Eastern coals) and PSOC 1323 (IL #6, hvBb) stands alone as the one with relatively high sulfate sulfur. The rest of the seven coals are not high in any form of sulfur. In order to achieve a better understanding of how different forms of sulfur influence the composition of sulfur containing molecules in the products, canonical correlations were performed between the MS data sets on the coal and tar samples listed in Table 2. Details of this procedure are provided elsewhere (Chakravarty, Khan and Mauzelaar, 1989b). Canonical correlation assesses the relationship between two or more sets of factors (independent characteristic directions in a data set) on the basis of accounting for a maximum overlap between the two sets of underlying variables. Two significant canonical variates

(correlation coefficient  $>0.9$ ) were found describing respectively 64% and 58% of the variance in the coal and the tar sets. Figures 1 and 2 describe the sample scores in the space of canonical variate 1 (CV1) and variate 2 (CV2). As we can see the two score plots are alike in terms of their topography (relative location of samples in the space). This means that with respect to the underlying variables (Table 2), the coal samples and the corresponding tars are similar. In other words, the distribution of the twelve sulfur variables will be similar in a tar from a given coal.

The following observation was also aided by numerically extracted spectra. Specifically, we observed that more thiophenes, thionaphthenes and dibenzothiophenes are present in hvAb coals (group of samples at the bottom left marked by circle; Figure 1) and are transferred to the corresponding tars. Our data confirm that coals with high organic sulfur contribute to high aromatic sulfur. This finding, however, is based on a limited data set. Based on the same arguments, the gases (noncondensables at the temperature of MS detector, close to room temperature) from the hvAb coals are expected to contain more aromatic sulfur. Unlike the hvAb coals, the lower rank coals have characteristically lesser  $m/z$  184 (dibenzothiophene) than  $m/z$  134 (thionaphthenes).

The tars from the lower rank coals (hvCb) [Figure 2] show predominantly more hydrogen sulfide, mercaptans and elemental sulfur, except for the IL#6 (hvBb) coal which yields less hydrogen sulfide. For all these coals we note relatively greater amounts of alkyl sulfides. IL #6 coal differs from other lower rank coals in that it also has a high proportion of sulfate sulfur.

#### Devolatilization of coal using a heated-grid reactor

Tables 3 and 4 provide a summary of results regarding the pyrolysis products generated using a heated-grid reactor. Characterization data such as these are of interest as these coals have been gasified in large scale at the Texaco Coal Gasification Processes (at the Montebello Research Lab and at Cool Water). One obvious conclusion that can be made regarding these results is that the yield of gaseous sulfur products from the Sufco coal is significantly lower than that observed for the Illinois No. 6 coal. Additional analyses of these results will be presented in a future report when further information on sulfur chemistry is generated.

#### **SUMMARY AND CONCLUSIONS**

The following conclusions can be drawn based on this study: (a) Advanced statistical techniques appear to be useful to classify coals according to their sulfur type (shown by factor analysis). (b) CV1 and CV2 (results of canonical correlations) space of the pyrolyzed coal and evaporated tar samples indicate that the sulfur distribution relationships between the coals and the

corresponding evaporated tars prepared from the same coals in a fixed-bed reactor follow similar patterns. (c) The upper block Indiana Coal (No. 18, sub-bituminous A), although a lower rank coal, is different in terms of its sulfur constituents than the other (Nos. 8, 19, 23) lower rank coals. (d) The IL#6 (No. 23; hvAb) coal with high pyritic and sulfate sulfur also has high hydrogen sulfide content in the pyrolyzed coal and relatively low hydrogen sulfide in the evaporated tar spectrum. (e) Relatively more thiophenes, thionaphthenes and dibenzothiophenes are present in the hvAb coal and are transferred to the corresponding tars. (f) Results indicate that all lower rank coals have less dibenzothiophenes ( $m/z$  184) than thionaphthene ( $m/z$  134), unlike hvAb coals, and more elemental sulfur. (g) The tars from high volatile coals (hvAb) coals appear to contain lower amounts of aromatic sulfur whereas the tars from the low volatile (hvCb) coal appear to have small amounts of alkyl sulfides. Additional analyses on the influence of devolatilization conditions on sulfur evolution will be presented in a future report.

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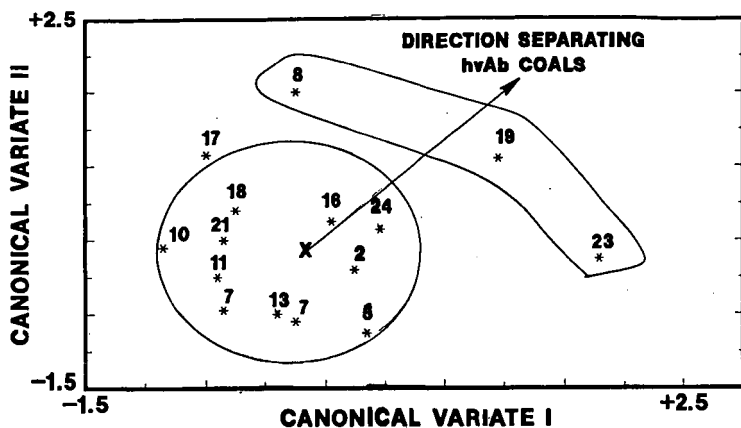


Figure 1 Score plot in CV1/CV2 space obtained from Canonical Correlation Analysis of MS data and on sulfur masses between coals and tars. Note the clustering of groups of pyrolyzed coal samples according to coal rank. The close proximity of PSOC 181 (sub bit A) coal with other hvAb coals could be attributed to relatively higher organic sulfur content of this coal.

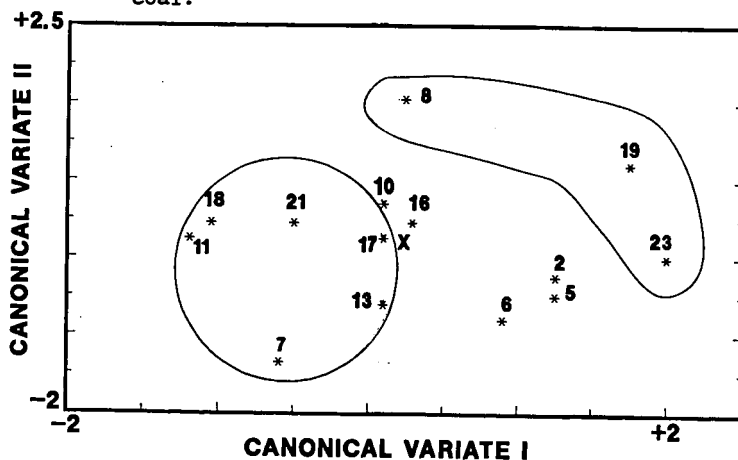


Figure 2 Score plot in CV1/CV2 space obtained from Canonical Correlation Analysis of MS data and on sulfur masses between coals and tars. Note the clustering of groups of tar samples similar to coals based on sulfur containing masses. The close proximity of the tar sample obtained from PSOC 181 (sub bit A) coal with other hvAb coals could be again attributed to relatively high organic sulfur (with no sulfate or pyritic sulfur) of this coal.

**Table 1      Influence of Coal Sulfur Type on Sulfur Distribution in Products**

**Influence of Coal Sulfur Type on Sulfur Distribution in Gaseous Products**

	<u>R<sup>2</sup></u>
Total Sulfur in Gas $\equiv 0.43$ (Coal <sub>pys</sub> )	0.68
$\equiv 0.63$ (Coal <sub>orgs</sub> )	0.86
$\equiv 0.22$ (Coal <sub>pys</sub> ) + 0.46 (Coal <sub>orgs</sub> )	0.96
[H <sub>2</sub> S] $\equiv 0.36$ (Coal <sub>pys</sub> )	0.65
$\equiv 0.53$ (Coal <sub>orgs</sub> )	0.86
$\equiv 0.17$ (Coal <sub>pys</sub> ) + 0.40 (Coal <sub>orgs</sub> )	0.94
[COS] $\equiv 0.071$ (Coal <sub>pys</sub> )	0.75
$\equiv 0.095$ (Coal <sub>orgs</sub> )	0.81
$\equiv 0.040$ (Coal <sub>pys</sub> ) + 0.063 (Coal <sub>orgs</sub> )	0.96

**Influence of Coal Sulfur Type on Sulfur Distribution in Tar**

	<u>R<sup>2</sup></u>
Total Sulfur in Tar $\equiv 0.0128$ (Coal <sub>pys</sub> )	0.58
$\equiv 0.123$ (Coal <sub>orgs</sub> )	0.82
$\equiv 0.034$ (Coal <sub>pys</sub> ) + 0.095 (Coal <sub>orgs</sub> )	0.88

**Influence of Coal Sulfur Type on Sulfur Distribution in Char**

	<u>R<sup>2</sup></u>
Total Sulfur in Char $\equiv 0.95$ (Coal <sub>pys</sub> )	0.88
$\equiv 1.09$ (Coal <sub>orgs</sub> )	0.69
$\equiv 0.70$ (Coal <sub>pys</sub> ) + 0.53 (Coal <sub>orgs</sub> )	0.98



Table 2

pyritic S  
organic S  
sulfate S

**Table 3**  
SUMMARY OF PYROLYSIS YIELDS IN HGR FOR ILLINOIS #6 (WT% OF DRY COAL)

ILL. #6	Slow Pyrolysis									
	30	31	17	18	19	25	23	26		
Run #	Grid	Grid	Grid	Grid	Grid	Grid	Grid	Grid		
Geometry	1000	1000	600	800	1500	700	1000	1500		
Peak Temperature (°C)	0	0	20	15	4	25	10	4		
Hold Time (sec)	15	15	150	400	1333.3	233.3	500	1333.3		
Heating Rate (°C/sec)	1.5	1.5	VAC	VAC	VAC	2.5	2.5	2.5		
Pressure	1.0	1.0	61.1	76.6	62.0	63.8	64.2	62.1		
Sample Amount (mg)	170.3	141.7	61.1	76.6	62.0	63.8	64.2	62.1		
Flow Rate (l/min)	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7		
Mesh Size	(40-60)	(40-60)	(60-100)	(60-100)	(60-100)	(40-60)	(40-60)	(40-60)		
PYROLYSIS DISTRIBUTION										
Char	73.0	66.8	77.3	69.2	41.5	77.0	71.2	55.4		
Tar	10.3	10.5	14.4	17.5	30.8	18.0	8.9	7.4		
Dry Gas	12.2	10.3	4.8	8.1	17.3	9.5	14.3	35.3		
Water	2.6	1.0	1.6	2.5	2.5	1.9	1.6	1.6		
Missing	1.9	11.4	1.9	2.7	7.9	-6.4	4.0	0.3		
Tar + Missing	12.2	21.8	16.3	20.2	38.7	11.6	12.9	7.7		
GAS COMPOSITION										
CH <sub>4</sub>	2.55	2.35	1.16	1.90	1.15	1.90	2.68	1.16		
H <sub>2</sub>	3.50	3.40	.30	1.37	8.16	1.81	4.70	18.62		
N <sub>2</sub>	0	0	.03	.74	2.27	2.29	0	0		
Acetylene	3.50	1.61	.53	.49	.22	0	2.71	2.00		
Ethylene	0	0	.01	.01	.69	0.22	0.51	0.82		
Ethane	.22	.16	.14	.22	.47	0.22	0.51	0.82		
Propylene	0.34	0.53	.52	.58	.47	0.18	0.40	0.40		
Propylene	0	.30	.20	.22	.26	0.18	0.23	0.04		
Benzene	0	0	0	0	0	0	0	0		
Paraffins	1.32	1.52	1.71	1.50	1.17	2.40	1.96	0		
Olefins	0	0	.09	.55	1.15	0	0.67	0		
HCN	0.22	0.25	.08	.51	1.20	0.07	0.32	2.58		
Azonla	0	1.01	0	0	0	0	0	0		
CUS	0	0	0	0	0	0.01	0.01	0		
CS <sub>2</sub>	0.64	0.61	0	.02	.03	0.08	0.04	0.30		
S0 <sub>2</sub>	0	0.01	.05	.03	.01	0.04	0.04	0.01		
H <sub>2</sub> O	2.6	1.0	1.61	2.5	2.5	1.9	1.64	1.62		
GAS TOTAL	14.89	12.79	6.42	10.64	19.82	11.41	15.95	27.19		

Table 4

SUMMARY OF PYROLYSIS YIELDS IN MGR FOR SUFCO (WT% OF DRY COAL)

SuFCO		Slow Pyrolysis				
Run #	29	32	24	22	21	
Geometry	Grid	Grid	Grid	Grid	Grid	
Peak Temperature (°C)	1000	1000	700	1000	1500	
Hold Time (sec)	0	0	25	10	4	
Heating Rate (°C/sec)	.5	.5	33.3	500	1333.3	
Pressure	1 ATM	1 ATM	2 ATM	2 ATM	2 ATM	
Sample Amount (mg)	148.5	189.3	67.4	53.1	64.5	
Flow Rate (l/min)	.7	.7	0	0	0	
Mesh Size	(40-60)	(100-200)	(40-60)	(40-60)	(40-60)	
PYROLYSIS DISTRIBUTION						
Char	65.5	64.8	65.1	59.5	50.4	
Tar	2.3	2.7	10.4	8.3	8.5	
Dry Gas	16.2	13.5	15.6	30.1	31.0	
Water	1.8	1.0	2.0	2.0	1.0	
Missing	14.2	17.3	6.9	0.1	9.1	
Tar + Missing	16.5	20.0	17.3	8.4	17.6	
GAS COMPOSITION						
CH <sub>4</sub>	2.56	2.40	2.29	3.37	2.50	
CO	4.44	4.14	3.13	8.72	17.62	
H <sub>2</sub>						
CO <sub>2</sub>	5.2	4.10	3.90	7.25	3.44	
Acetylene	0	0	0	0.07	1.35	
Ethylene	0.16	0.20	0.41	1.54	0.83	
Ethane	0.54	0.30	0.54	0.58	0	
Propylene	0.30	0	0.47	1.10	0.28	
Benzene	0	0	0	0	0	
Paraffins	2.27	2.18	3.77	3.30	0	
Olefins	0	0	0.79	3.56	1.19	
HCN	0.29	0.19	0.20	0.35	3.68	
Ammonia	0.02	0.01	0.01	0.02	0	
COS	0	0	0	0	0	
CS <sub>2</sub>	0.48	0.48	.08	0.23	0.10	
SO <sub>2</sub>	0	0	0	0	0	
H <sub>2</sub> O	1.8	1.0	2.0	2.0	1.0	
GAS TOTAL	18.6	15.0	17.59	32.09	31.99	